

AD-A206 589

JRT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS														
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited														
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 89-0389														
4a. NAME OF PERFORMING ORGANIZATION M.I.T. Department of Chemistry		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION AFOSR/NC													
6c. ADDRESS (City, State and ZIP Code) Cambridge, MA 02139		7b. ADDRESS (City, State and ZIP Code) Bldg 410 Bolling Air Force Base, DC 20332															
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR		8b. OFFICE SYMBOL (If applicable) NC		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-85-0265													
8c. ADDRESS (City, State and ZIP Code) Building 410 Bolling Air Force Base, DC 20332		10. SOURCE OF FUNDING NOS. <table border="1"><thead><tr><th>PROGRAM ELEMENT NO.</th><th>PROJECT NO.</th><th>TASK NO.</th><th>WORK UNIT NO.</th></tr></thead><tbody><tr><td>61102F</td><td>2303</td><td>B2</td><td></td></tr></tbody></table>				PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.	61102F	2303	B2					
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61102F	2303	B2															
11. TITLE (Include Security Classification) Organosilicon Compounds and Polymers and Silicon Ceramics																	
12. PERSONAL AUTHOR(S) Dietmar Seyferth																	
13a. TYPE OF REPORT Final Scientific		13b. TIME COVERED FROM 10/1/85 TO 10/31/88		14. DATE OF REPORT (Yr., Mo., Day) 39 Mar 2													
				15. PAGE COUNT 12													
16. SUPPLEMENTARY NOTATION																	
17. COSATI CODES <table border="1"><thead><tr><th>FIELD</th><th>GROUP</th><th>SUB. GR.</th></tr></thead><tbody><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></tbody></table>			FIELD	GROUP	SUB. GR.										18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) preceramic polymers polycarbosilanes, polysilanes, silicon carbide. (A)		
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) 1. The n-BuLi/Me ₃ COK reagent metalates every fourth CH ₂ group of [(CH ₃) ₂ SiCH ₂] _n . The metalated polymer was converted to vinyl-containing polycarbosilanes whose reaction with [(CH ₃ SiH) _x (CH ₃ Si) _y] _n gave useful preceramic polymers. 2. Cross-linkable [CH ₃ (H)SiCH ₂] _n has been prepared using [CH ₃ (Ph)SiCH ₂] _n as starting material. 3. The reactions of [(CH ₃ SiH) _x (CH ₃ Si) _y] _n with Cp ₂ MMe ₂ (M= Ti, Zr, Hf) gave precursors for SiC/MC blends. 4. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane can be metalated with t-BuLi/TMEDA. 5. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane can be metalated with t-BuLi/TMEDA. 6. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane can be metalated with t-BuLi/TMEDA.																	
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input checked="" type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION Unclassified														
22a. NAME OF RESPONSIBLE INDIVIDUAL A.J. Matuszko		22b. TELEPHONE NUMBER (Include Area Code) (202) 767-4963		22c. OFFICE SYMBOL NC													

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COMPLETED PROJECT SUMMARY

1. TITLE: Organosilicon Compounds and Polymers and Silicon Ceramics
2. PRINCIPAL INVESTIGATOR: Prof. Dietmar Seyferth
Dept. of Chemistry, Room 4-382
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
3. INCLUSIVE DATES: 1 October 1985 - 31 October 1988
4. GRANT NO.: AF-AFOSR-85-0265
5. COST AND FY SOURCE:

6. SENIOR RESEARCH PERSONNEL: H. Lang
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H.J. Tracy
J.L. Robinson
R.C. Hui

Accession For	
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DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

8. PUBLICATIONS:

"The Preparation of Silicon-Containing Ceramics via Polymeric Organosilicon Precursors", D. Seyferth. *L'actualité chimique*, 71 (March) 1986.

"Organosilicon Polymers as Precursors for Silicon-Containing Ceramics: Recent Developments", D. Seyferth, G.H. Wiseman, C.A. Poutasse, J.M. Schwark and Y.-F. Yu. *Polymer Preprints*, 28 (1987) 389.

"Polycarbosilanes: An Overview", D. Seyferth. Chapter in "Inorganic and Organometallic Polymers" (ACS Symposium Series 360), M. Zeldin, K.J. Wynne and H.R. Allcock, editors, American Chemical Society, Washington, D.C., 1988.

"A Novel Polymeric Organosilazane Precursor to $\text{Si}_3\text{N}_4/\text{SiC}$ Ceramics", D. Seyferth and G.H. Wiseman. In "Science of Ceramic Chemical Processing", L.L. Hench and D.R. Ulrich, editors, Wiley, New York, 1986, Chapter 38, pp. 354-362.

"The Preceramic Polymer Route to Silicon-Containing Ceramics", D. Seyferth and Y.-F. Yu. In "Design of New Materials", D.L. Cocke and A. Clearfield, editors, Plenum Press, New York, 1987, pp. 79-94.

"Methyldichlorosilane in the Service of Materials Science", D. Seyferth. In "Ultrastructure Processing of Advanced Ceramics", J.D. Mackenzie and D.R. Ulrich, editors, Wiley, New York, 1988, pp. 33-39.

"Organosilicon Polymers as Precursors for Silicon-Containing Ceramics. Recent Developments", D. Seyferth, G.H. Wiseman, J.M. Schwark, Y.-F. Yu and C.A. Poutasse. In "Inorganic and Organometallic Polymers" (ACS Symposium Series 360), M. Zeldin, K.J. Wynne and H.R. Allcock, editors, American Chemical Society, Washington, D.C., 1988, pp. 143-155.

"Applications of Methyldichlorosilane in Preparation of Silicon-Containing Ceramics", D. Seyferth, G.H. Wiseman, Y.-F. Yu, T.S. Targos, C.A. Sobon, T.G. Wood and G.A. Koppetsch. In "Silicon Chemistry", J.Y. Corey and P.P. Gaspar, editors, Ellis Horwood, Chichester, 1988, pp. 415-424.

"Organosilicon Polymers as Precursors for Silicon-Containing Ceramics", D. Seyferth. In "Transformation of Organometallics Into Common and Exotic Materials: Design and Activation", (NATO ASI Series E, Applied Sciences, No. 141), R.M. Laine, editor, Martinus Nijhoff Publishers, Dordrecht, 1988, pp. 133-154.

9. ABSTRACT AND OBJECTIVES AND ACCOMPLISHMENTS

a. The $n\text{-BuLi}/\text{Me}_3\text{COK}$ reagent metalates every fourth CH_2 group of $[(\text{CH}_3)_2\text{SiCH}_2]_n$. The metalated polymer was converted to vinyl-containing polycarbosilanes whose reaction with $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ gave useful preceramic polymers.

b. Cross-linkable $[\text{CH}_3(\text{H})\text{SiCH}_2]_n$ has been prepared using $[\text{CH}_3(\text{Ph})\text{SiCH}_2]_n$ as starting material.

c. The reactions of $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ with Cp_2MMe_2 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) gave precursors for SiC/MC blends.

d. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane can be metalated with $t\text{-BuLi}/\text{TMEDA}$.

AFOSR-TR. 89-0389

FINAL SCIENTIFIC REPORT

Grant No. AF-AFOSR-85-0265

"Organosilicon Compounds and Polymers and Silicon Ceramics"

Principal Investigator: Professor Dietmar Seyferth

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

March 2, 1989

Approved for public release;
distribution unlimited.

A. Period Covered and Personnel

1. Period Covered

1 October 1985 - 31 October 1988

2. Personnel

(Personnel are listed whose salaries and/or research costs were covered totally or in part by this Grant.)

a. Principal Investigator

Dietmar Seyferth, Professor of Chemistry

b. Postdoctoral Investigators

H. Lang (Univ. of Konstanz)

J. Borm (Univ. of Konstanz)

M.J. Michalczyk (Univ. of Wisconsin)

G. Koppetsch (Max-Planck-Institut für Kohlenforschung,
Mülheim/Ruhr)

T.S. Targos (Pennsylvania State University)

B. Neumüller (Univ. of Stuttgart)

W. Bernhardt (Univ. of Freiburg)

c. Predoctoral Investigators

C.A. Sobon

H.J. Tracy

J.L. Robison

R.C. Hui (Ph.D.)

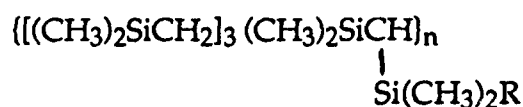
B. Research Accomplishments

All of the research has been devoted to the synthesis and evaluation of organosilicon preceramic polymers.

1. Polycarbosilane Synthesis and Modification

a. Chemistry Based on $[(CH_3)_2SiCH_2]_n$

The $[(CH_3)_2SiCH_2]_n$ polycarbosilane is obtained by literature procedures by the chloroplatinic acid-catalyzed ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Its pyrolysis under argon gives zero ceramic yield. We have functionalized this polymer by metalation of its CH_2 bridges (about every fourth CH_2 group) with the strongly basic n -BuLi/ $(CH_3)_3COK$ reagent to give $\{[(CH_3)_2SiCH_2]_3(CH_3)_2SiCHK\}_n$. Reactions of the latter with the appropriate chlorosilane, $(CH_3)_2RSiCl$, were used to prepare polycarbosilanes with functional side-chains:



(R = H and $CH_2=CH$)

A useful polymeric precursor for SiC was prepared by the reaction of the polymer where R = $CH_2=CH$ with the polysilane $[(CH_3SiH)_x(CH_3Si)_y]_n$. Si-H addition to the $CH_2=CH$ groups (AIBN catalyst) resulted in an extensively cross-linked, but still soluble organosilicon polymer. By using the appropriate amounts of each polymer, a preceramic material could be obtained whose pyrolysis to $1000^\circ C$ under argon gave a ceramic residue that by elemental analysis was greater than 95% SiC.

b. Synthesis of $[CH_3(H)SiCH_2]_n$

By ring-opening polymerization of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane polymers of type $H[Ph(CH_3)SiCH_2]_nSiEt_3$ ($n = 26 - 44$)

were prepared. (Small amounts of Et_3SiH were present in the reaction mixture to limit chain growth.) Brominolysis resulted in selective cleavage of up to 97% of the phenyl groups from silicon, leaving the methyl substituents in place. The brominated polymer was converted to those derivative polymers in which the Si-Br function had been replaced by Si-H (reaction with LiAlH_4), Si-CH=CH₂ (reaction with vinylmagnesium bromide) and Si-N₃ (reaction with NaN_3). In terms of promise as measured by good ceramic yield obtained on pyrolysis, hybrid polymers obtained by AIBN-catalyzed reaction of the Si-H substituted polycarbosilane with cyclo-[(CH₃)(CH₂=CH)SiNH]₃ and of the vinyl-substituted polycarbosilane with the [(CH₃SiH)_x(CH₃Si)_y]_n polysilane are worth following up.

c. [(CH₃(R)SiC≡C)]_n

Relatively low molecular weight polymers in which R = H and CH₂=CH were prepared by reaction of [MgC≡C]_n with the appropriate CH₃(R)SiCl₂ compound. Pyrolysis of such polymers gives SiC, but a high yield of elemental carbon also is obtained. However, hybrid polymers prepared by reaction of [(CH₃)(CH₂=CH)SiC≡C]_n with the polysilane [(CH₃SiH)_x(CH₃Si)_y]_n in the right proportions gave, on pyrolysis to 1000°C a ceramic residue containing Si and C in very close to 1:1 ratio. Such systems are receiving further study.

2. Ceramic Yield Enhancement and Transition Metal Incorporation by Reaction of Si-H Containing Polymers with Metal Carbonyls

Organosilicon polymers containing a multiplicity of Si-H functions can be "up-graded" by appropriate Si-H chemistry, as we have shown previously in AFOSR-sponsored research. One such Si-H containing polymer is the Nicalon polycarbosilane which contains the CH₃(H)SiCH₂ unit as a major repeat unit. Pyrolysis of uncured Nicalon polycarbosilane gives

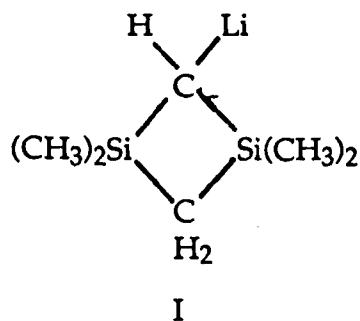
ceramic residue yields on the order of 55-60%. By means of the photolytic reaction of this polymer with 2 weight % of $\text{Ru}_3(\text{CO})_{12}$ we have been able to increase the ceramic yield to over 80%. By reaction with Si-H bonds the $\text{Ru}_3(\text{CO})_{12}$ cross-links the polycarbosilane to an extent greater than before this reaction; ruthenium is incorporated into the polymer. Reactions in which $\text{Fe}_3(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ were used gave similar results. Similar "up-grading" in terms of ceramic yield was observed with the polysilane $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ (liquid PS increased from 12 to 55% in ceramic yield on photolysis with 2 weight % of $\text{Ru}_3(\text{CO})_{12}$; solid PS increased from 52 to 73%). Such $\text{Ru}_3(\text{CO})_{12}$ /UV treatment of mixtures of the Nicalon polycarbosilane and the above-mentioned polysilane in the appropriate ratio gave new organosilicon polymers whose pyrolysis resulted in ceramic residues in good yield that by analysis were up to 99% SiC. A patent disclosure has been written on this work.

3. Another Approach to Ceramic Blends

The biscyclopentadienyldimethyl derivatives of Ti, Zr and Hf react with the $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ polysilanes to give, under appropriate conditions, soluble hybrid polymers that contain silicon and the other metal. Pyrolysis of these new polymers leaves a ceramic residue that contains SiC and TiC (or ZrC or HfC) plus substantial amounts of free carbon. Such polymers may be suitable for the pyrolytic formation of protective SiC/MC ceramic coatings on carbon/carbon composites. More work is required to understand the chemistry involved in the synthesis of these materials.

4. Small Molecule Chemistry: the Metalation of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane

The above-mentioned cyclic carbosilane can be metalated with the $t\text{-BuLi} \cdot \text{tetramethylethylenediamine}$ reagent to give



Studies are underway to develop the chemistry of this novel reagent.

C. Publication List

1. The Preparation of Silicon-Containing Ceramics via Polymeric Organosilicon Precursors.
L'actualité chimique, 71 (March) 1986
D. Seyferth
2. Organosilicon Polymers as Precursors for Silicon-Containing Ceramics: Recent Developments.
Polymer Preprints, 28 (1987) 389
D. Seyferth, G.H. Wiseman, C.A. Poutasse, J.M. Schwark and Y.-F. Yu
3. Polycarbosilanes: An Overview
Chapter in "Inorganic and Organometallic Polymers" (ACS Symposium Series 360), M. Zeldin, K.J. Wynne and H.R. Allcock, editors, American Chemical Society, Washington, D.C., 1988.
D. Seyferth
4. A Novel Polymeric Organosilazane Precursor to Si₃N₄/SiC Ceramics.
in "Science of Ceramic Chemical Processing", L.L. Hench and D.R. Ulrich, editors, Wiley, New York, 1986, Chapter 38, pp. 354-362.
D. Seyferth and G.H. Wiseman

5. The Preceramic Polymer Route to Silicon-Containing Ceramics
in "Design of New Materials", D.L. Cocke and A. Clearfield, editors, Plenum Press, New York, 1987, pp. 79-94.
D. Seyferth and Y.-F. Yu
6. Methylchlorosilane in the Service of Materials Science
in "Ultrastructure Processing of Advanced Ceramics", J.D. Mackenzie and D.R. Ulrich, editors, Wiley, New York, 1988, pp. 33-39.
D. Seyferth
7. Organosilicon Polymers as Precursors for Silicon-Containing Ceramics. Recent Developments.
in "Inorganic and Organometallic Polymers" (ACS Symposium Series 360), M. Zeldin, K.J. Wynne and H.R. Allcock, editors, American Chemical Society, Washington, D.C., 1988, pp. 143-155.
D. Seyferth, G.H. Wiseman, J.M. Schwark, Y.-F. Yu and C.A. Poutasse
8. Applications of Methylchlorosilane in Preparation of Silicon-Containing Ceramics.
in "Silicon Chemistry", J.Y. Corey and P.P. Gaspar, editors, Ellis Horwood, Chichester, 1988, pp. 415-424.
D. Seyferth, G.H. Wiseman, Y.-F. Yu, T.S. Targos, C.A. Sobon, T.G. Wood and G.A. Koppetsch
9. Organosilicon Polymers as Precursors for Silicon-Containing Ceramics
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D. Seyferth

D. Patents

1. Method for Forming New Preceramic Polymers for SiC and Si₃N₄/SiC Systems.
U.S. Patent 4,645,807 (February 24, 1987) - to M.I.T.
D. Seyferth, T.G. Wood and Y.-F. Yu

2. Method for Forming New Preceramic Polymers Containing Silicon.
U.S. Patent 4,639,501 (January 27, 1987)
D. Seyferth and Y.-F. Yu
3. Method for Converting Si-H Containing Polycarbosilanes to New and Useful Preceramic Polymers and Ceramic Materials.
U.S. Patent 4,650,837 (March 17, 1987)
D. Seyferth and Y.-F. Yu
4. Method for Converting Si-H Containing Polycarbosilanes to New and Useful Preceramic Polymers and Ceramic Materials.
U.S. Patent 4,705,837 (November 10, 1987)
D. Seyferth, Y.-F. Yu and T.S. Targos
5. Method For Forming New Preceramic Polymers Containing Silicon.
U.S. Patent 4,719,273 (January 12, 1988)
D. Seyferth, Y.-F. Yu and G.E. Koppetsch
6. Hybrid Polymers Derived From Si-H Containing Organosilicon Polymers and Unsaturated Metal Alkoxides.
U.S. Patent 4,780,337 (October 25, 1988)
D. Seyferth and T. Targos

E. Lectures Given by the Principal Investigator During the Grant Period

1985 (October - December)

8e Journées Scientifiques Rhône-Poulenc, Deauville (France)

Main group symposium, Deutsche Akad. der Wissenschaften
Leopoldina, Halle (DDR)

Hoechst AG, Frankfurt/Main (FRG)

Ultrastructure Conference on Organic and Inorganic Polymers. Amherst,
Massachusetts.

University of Oklahoma (Karcher Lecture)

Drew University, Madison, New Jersey

American Ceramic Society, Basic Sciences Division, Baltimore, Maryland

Dow Chemical New England Laboratory, Wayland, Massachusetts

Cornell University

CR&D Department, E.I. duPont

de Nemours & Co., Wilmington, Delaware

1986

Corning Glass Works, Corning, New York

University of Illinois

University of Connecticut

Texas A&M University
("Design of New Materials" Symposium)

Waters Chromatography Division, Millipore, Milford, Massachusetts

Tufts University

Ethyl Corp., Baton Rouge, Louisiana

169th Meeting, Electrochemical Society, Boston, Massachusetts

AT&T Bell Labs, Murray Hill, New Jersey

North American Philips Labs, Briarcliffmanor, New York

Nankai University, Tianjin, People's Republic of China

Hangzhou University, People's Republic of China

Shanghai Institute of Organic Chemistry, People's Republic of China

Gordon Research Conference on Organometallic Chemistry, Andover,
New Hampshire

Stauffer Research Labs, Dobbs Ferry, New York

Rhône-Poulenc St. Fons Research Center, Lyon (France)

NATO Workshop on Design, Activation and Transformation of Organo-
metallics into Common and Exotic Materials, Cap d'Agde (France)

University of Wisconsin, Madison

W.R. Grace Washington Research Center

1987

Third International Conference on Ultrastructure Processing of Ceramics,
Glasses and Composites, San Diego, California

193rd National ACS Meeting, Symposium on Inorganic and Organo-
metallic Polymers, Denver, Colorado

Eighth International Organosilicon Symposium, St. Louis, Missouri

Technical University of Berlin

194th National ACS Meeting: Committee on Science Symposium on
Chemical Problems in the Solid State

Oak Ridge National Laboratory
(Chemistry Division Distinguished Lecturer)

20° Congresso Nazionale di Chimica Inorganica, Pavia (Italy)
(Paulo Chini Memorial Lecturer)

University of Pennsylvania

"Frontiers in Organic Polymers", Philadelphia, Pennsylvania
(ACS Short Course)

ACS Division of Polymer Chemistry International Workshop on
Advances in Silicon-Based Polymer Science, Makaha, Oahu, Hawaii

1988 (through October 31)

University of Arizona

Joint Chemistry/Polymer Science and Engineering Special
Interdepartmental Seminar, University of Massachusetts, Amherst,
Massachusetts

Spring Meeting of the Materials Research Society, "Better Ceramics
Through Chemistry" Symposium, Reno, Nevada

Wesleyan University

Mobil Central Research Lab, Princeton, New Jersey

Armstrong World Industries, Lancaster, Pennsylvania

ALCOA Technical Center, Alcoa Center, Pennsylvania

Xerox Research Centre of Canada, Mississauga, Ontario

Joint Chemistry/Materials Science Colloquium, Iowa State University

"Frontiers in Inorganic Polymers", Philadelphia, Pennsylvania
(ACS Short Course)